

Energy Storage Research Group (ESRG)
Department of Materials Science and Engineering

Self-Forming Thin Interphases and Electrodes Enabling 3-D Structured High Energy Density Batteries

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***2019 DOE Vehicle Technologies Office
Annual Merit Review Presentation***

June 12, 2019



TARDEC Program Officer : Yi Ding

DOE VTO Technology Manager: Tien Duong

Project ID: ES323

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Timeline

- *Start Date:* October 01, 2016
- *End Date:* September 30, 2019
- **83% complete** as of April 1, 2019

Budget

- Total: \$ 1,271,165
- FY17 DOE : \$ 425,196
- FY18 DOE : \$ 317,544
- FY19 DOE: \$ 334,334
- 15% Cost Share

Partners



Barriers/Technical Targets

- **Performance:** Energy densities need to be improved to achieve weight and volume targets; 350 Wh/kg and 750 Wh/L at a cell level
- **Safety:** Abuse tolerance need to be improved under routine and extreme operating conditions
- **Cost:** Cost currently too high; target is a decrease by factor 3

Overall Objectives:

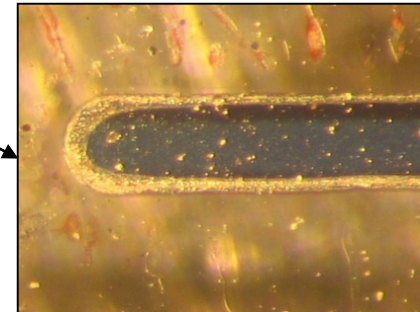
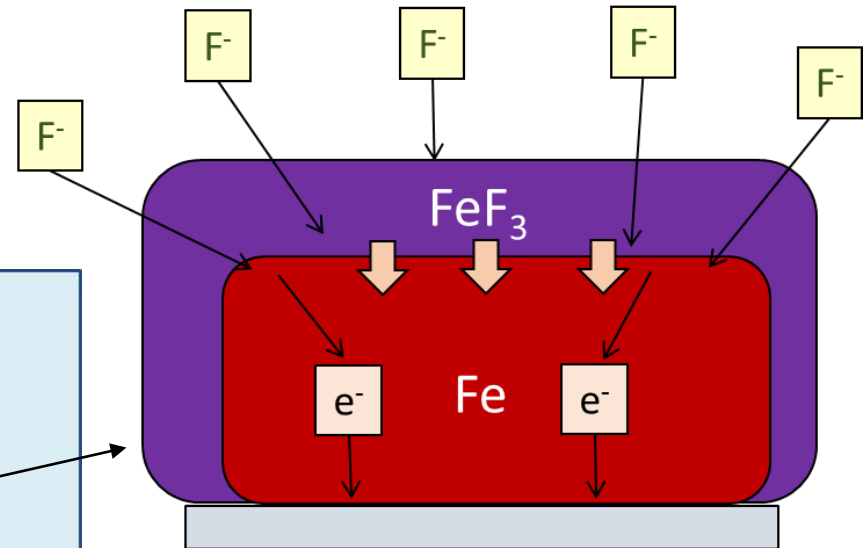
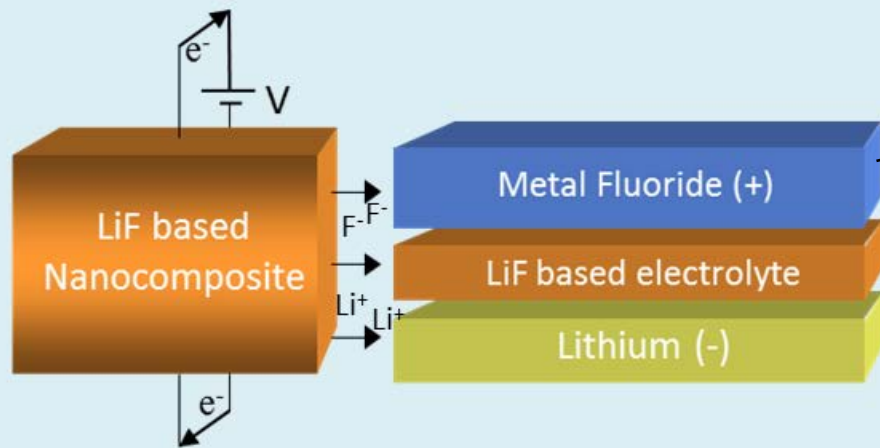
- Develop and implement a novel in-situ formed lithium metal-based metal fluoride battery
- Enable packaged 10 mAh batteries of energy densities $> 1000 \text{ Wh/L}$ and $> 400 \text{ Wh/kg}$ at 12 V within one planar unit

Current Period Objectives:

- Develop a small scale 12 V battery architecture to demonstrate the innate design flexibility of the electrolytically formed cell
- Quantify the effect of transport limitations on cell performance across the scale of the cell stack. Use the data in subsequent periods to guide the development of next generation product and use as input to validate models
- Increase the cycling stability and capacity retention for the 12 V architecture

- **Performance:** Highest practical energy density electrochemical system, above DOE-VT Office's targets
- **Performance:** Unique pathway to high voltage system enabling high energy density packaged cells, above DOE-VT Office's targets
- **Performance & Safety:** Non-flammable solid state electrolytes, would reduce abuse tolerance during shipping and operation
- **Safety & Cost:** Eliminate Li metal in fabrication and handling of cells, would improve shipping safety and reduce shipping and fabrication costs
- **Cost:** Mask-less, scalable patterning technique with potential for high throughput and low material loss fabrication would reduce costs of complex architecture fabrication
- **Cost:** Low cost materials

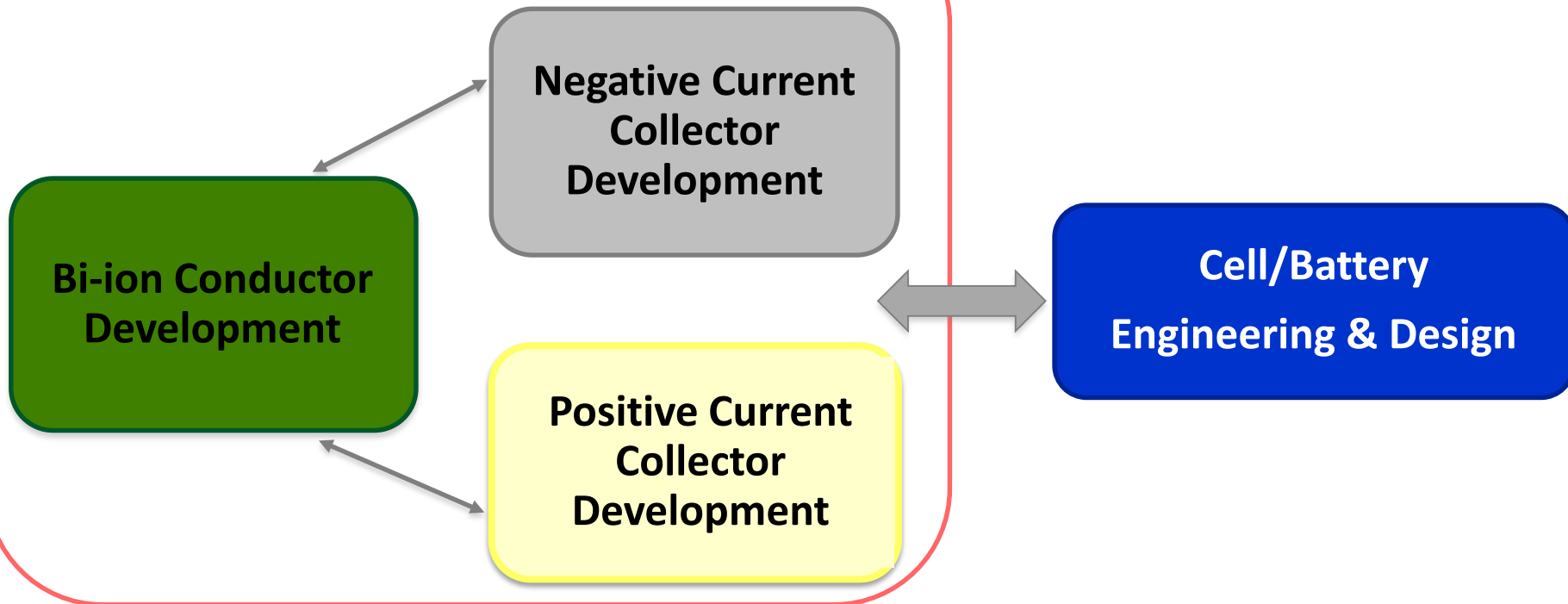
**Electrolytically Form
a Solid State Rechargeable Battery
From a Bi-ion Li-F-based Conductor**



- Challenges to be achieved by the end of FY19*

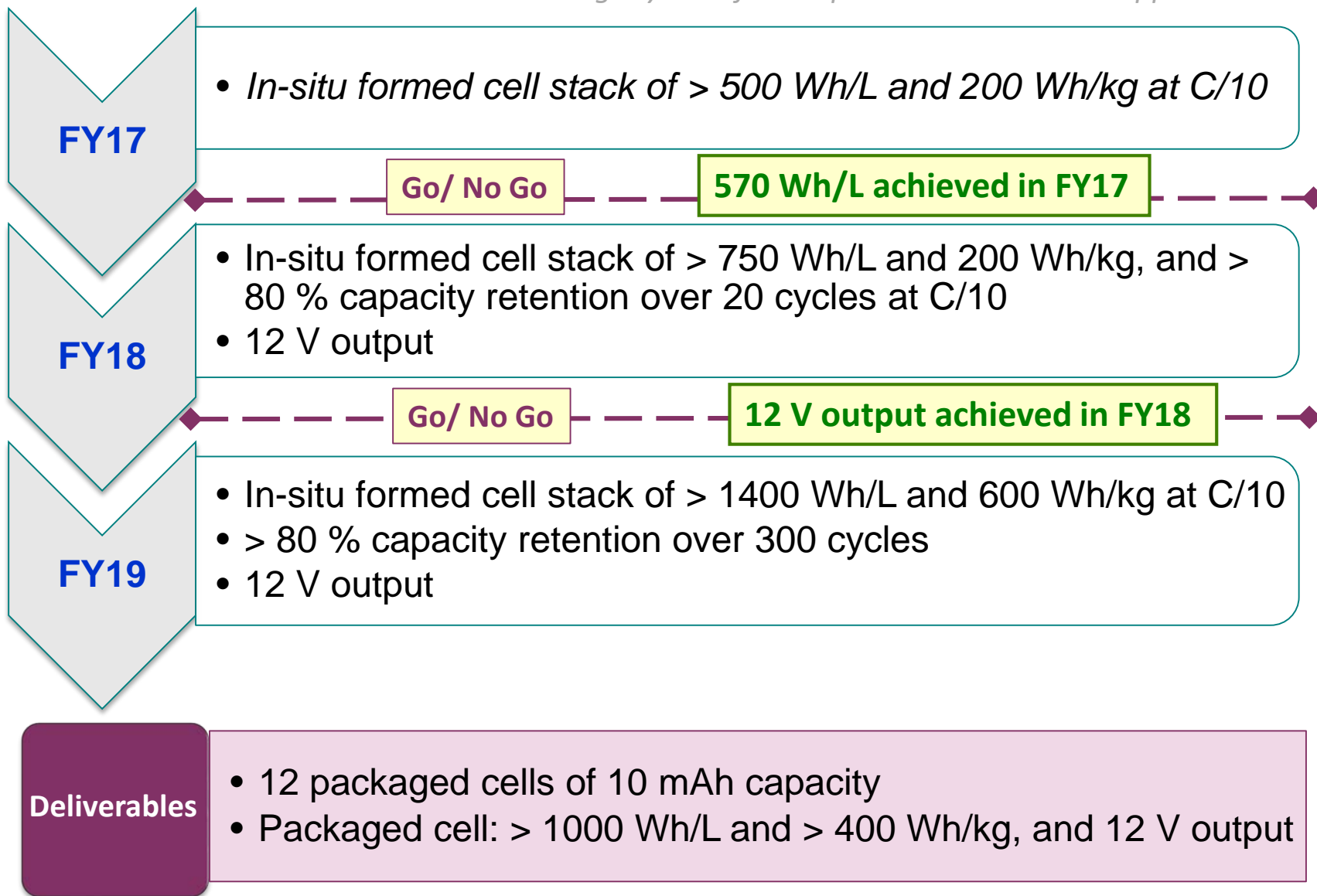
Milestone	Type	Description
Positive current collector development	Technical	Establish positive current collector compositions that achieve 90% of the theoretical energy density based on complete utilization of the initial amount of the positive reactive current collector.
Negative current collector development	Technical	Establish negative current collector compositions that enable high efficiency of lithium plating and stripping in excess of 95% during the in-situ formation step and >99% during subsequent cycles.
Bi-ion conductor development	Technical	Achieve <30% increase in electrolyte impedance after 50 cycles as characterized by Electrochemical Impedance Spectroscopy
Design and Fabrication; Electrodes and Cells	Technical	Design and fabricate 10 mAh cell stack that achieves 12V and delivers energy densities of 1400Wh/L and 600 Wh/kg per cell stack.

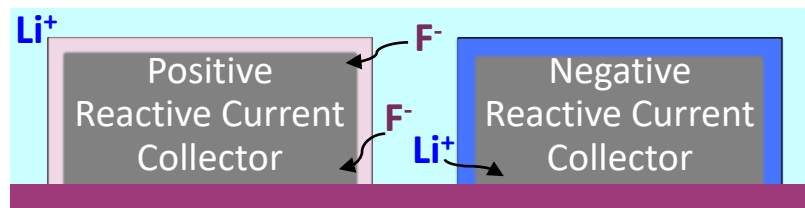
Cell chemistry Development/Optimization



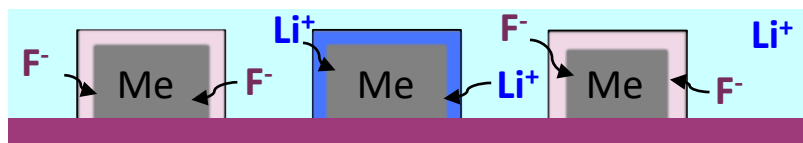
- ***Positive reactive current collector development:*** address composition and scalable fabrication approach
- ***Negative reactive current collector development:*** address composition and microstructure to facilitate rapid and uniform lithium deposition during the formation cycle and subsequent cycling
- ***Bi-ion solid-state conductor development:*** address LiF-based composition to enable facile electrolytic decomposition at the interface that will release the F^- and Li^+ ions to react with the positive and negative current collectors respectively thereby forming the cell in-situ, while maintaining fast ionic conductor of Li^+ to facilitate subsequent cycles

FY17 and FY18 Goals have been slightly modified as per our Continuation Applications

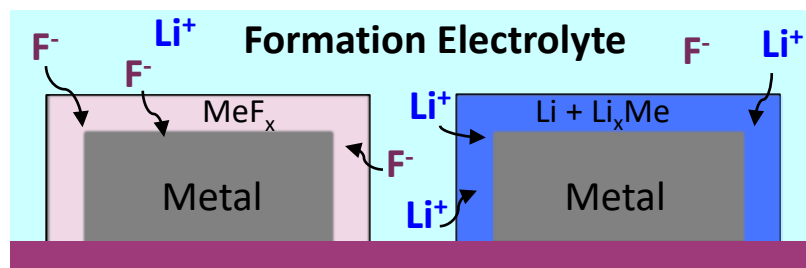




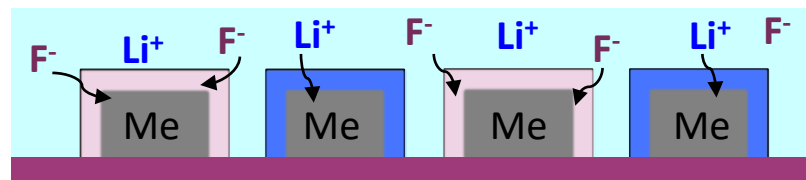
Standard Design:
No modifications - Benchmark



Modified Aspect Ratio:
Reactive current collectors with higher surface area to reduce diffusion distances



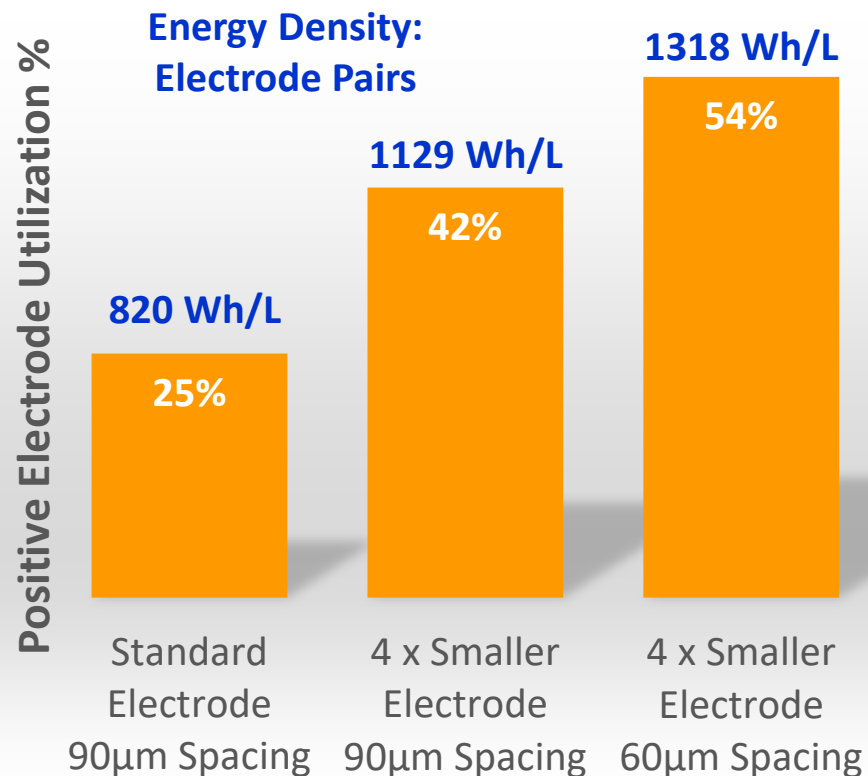
Excess Formation Electrolyte:
Excess F^- to ensure in-situ formation reactions not fluorine limited



**Excess Formation Electrolyte,
Modified Aspect Ratio
& Shorter Electrode Spacing:**
Smaller spacing width to further improve diffusion in addition to the two previous design modifications

Cell design evolution to
improve cell performance

Goal: Improve Electrode Utilization
Transport pathways play key role in capacity and utilization



Positive Electrode Active Discharge Capacity	Standard Electrode 90µm Spacing	4 x Smaller Electrode 90µm Spacing	4 x Smaller Electrode 60µm Spacing
Volumetric Capacity (mAh/cc)	474.1	861.0	1045.3

Better accessibility to the active material achieved by:

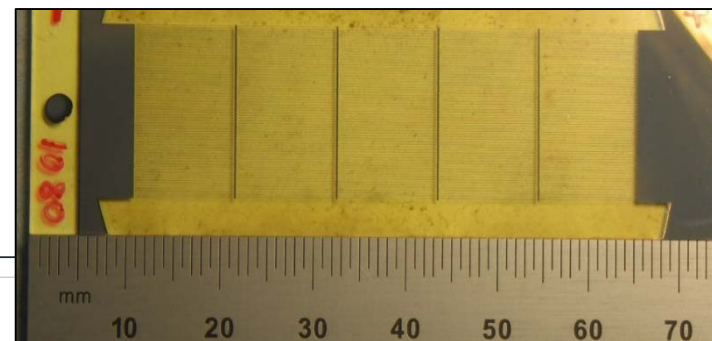
- Higher electrode surface area promoting better ionic/electronic interactions with the electrolyte
- Enhanced diffusion properties with decreased electrode spacing width

➔ Improve capacity and utilization

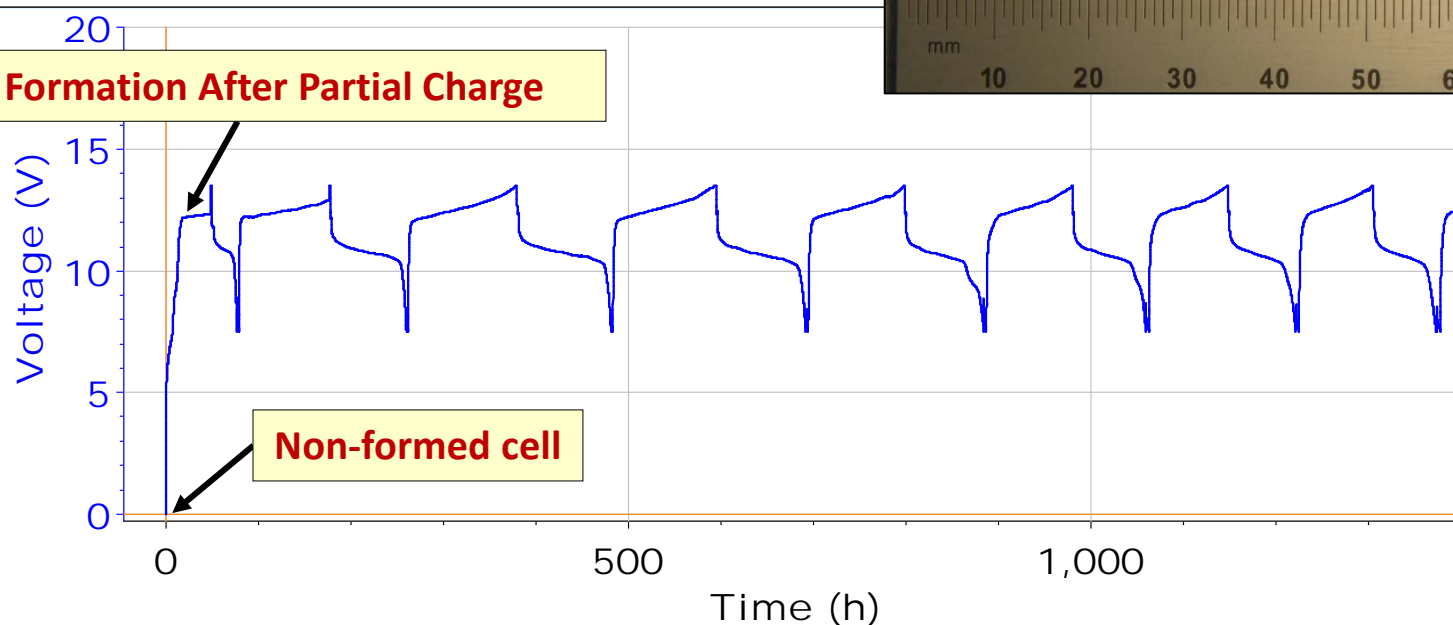
Reconfigurable design includes 64 cells in parallel & 5 sets in series = 320 cells total *Fabrication time: < 5 minutes*

Cycling of 12 V Cell: 7.5 to 13.5V

- Sequential charge capacity cutoffs 13 %, 26 %, 52 % of theoretical capacity in the first 3 cycles.; 52 % thereafter
- Discharge: CC 10nA, 100nA, 50nA with 15min rests



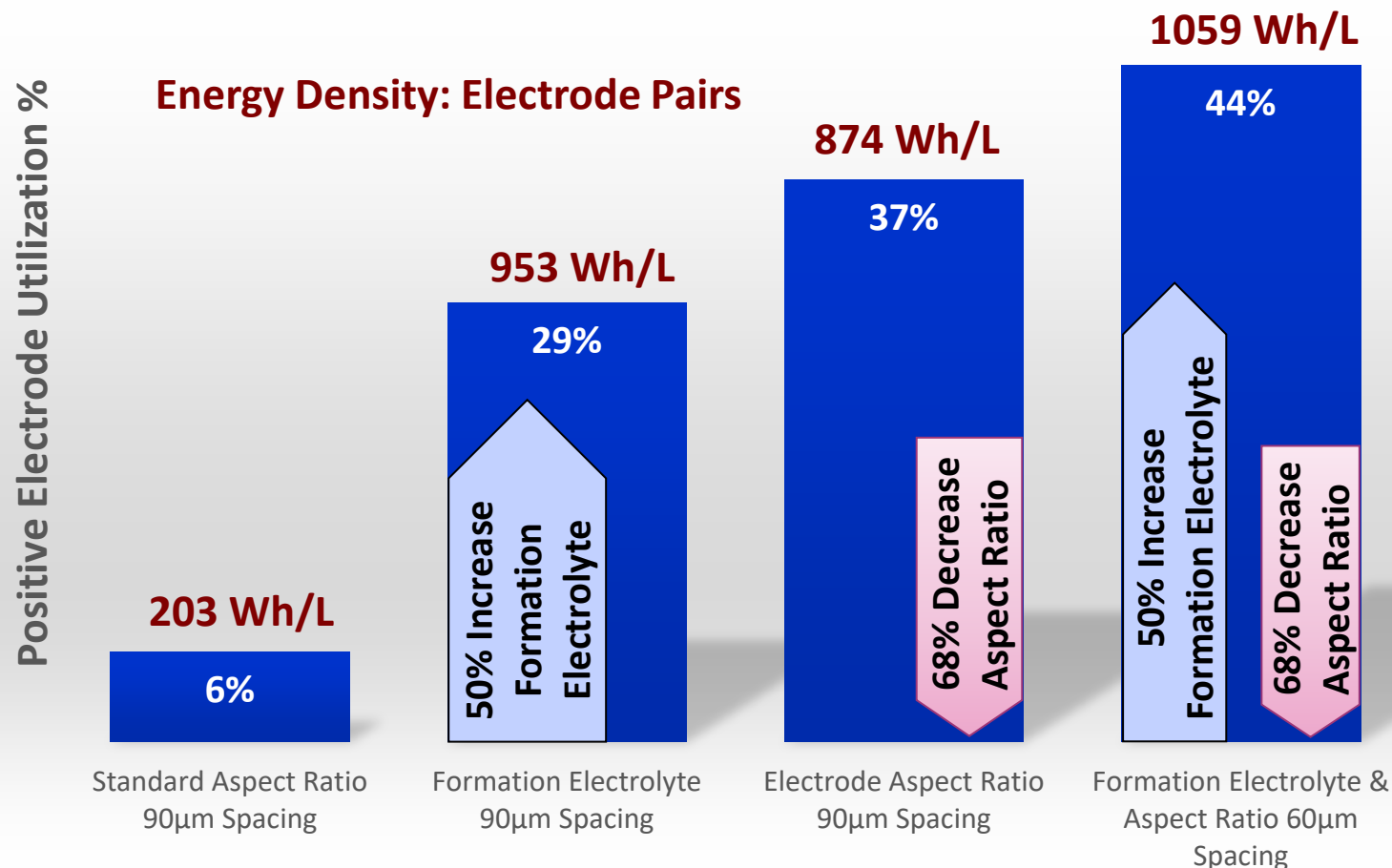
Cell Formation After Partial Charge



- ➔ Successful fabrication and in-situ formation of 12 V cell design
- ➔ High energy density in-situ formed electrode pairs of 855 Wh/L
- ➔ Cycling with minimal impedance buildup

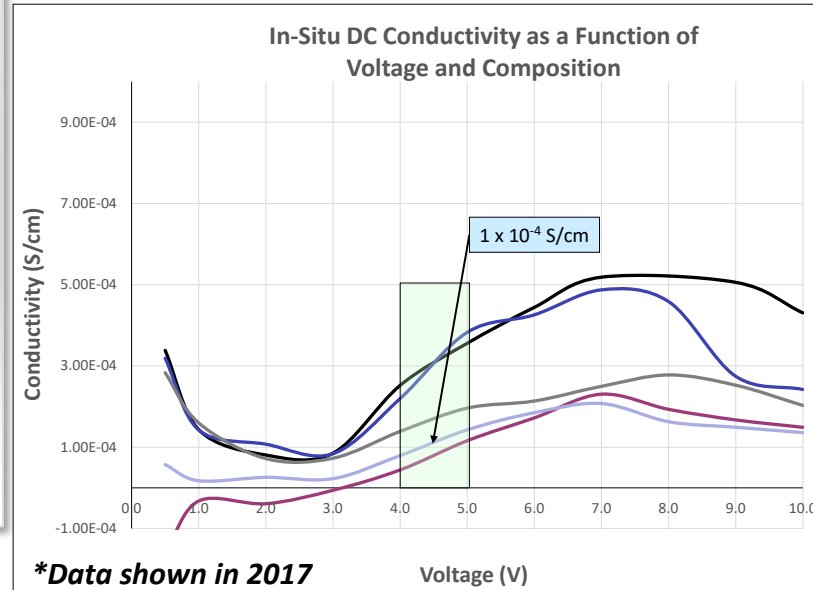
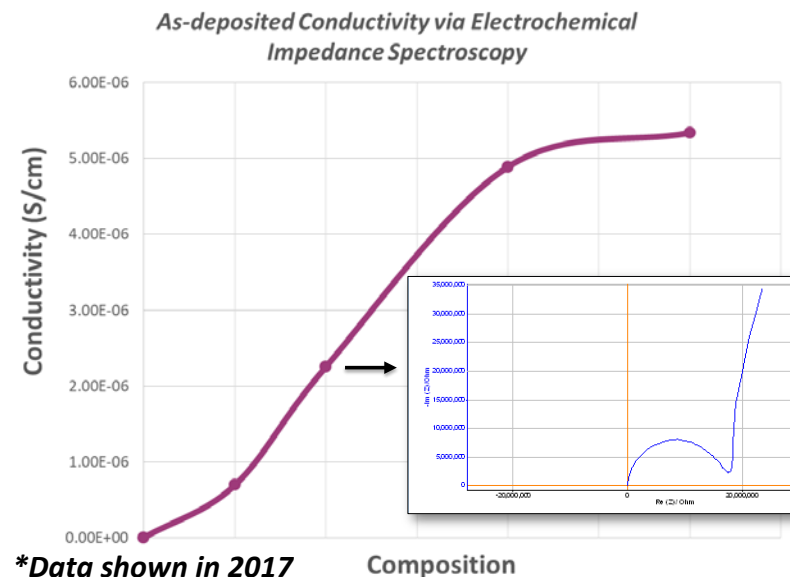
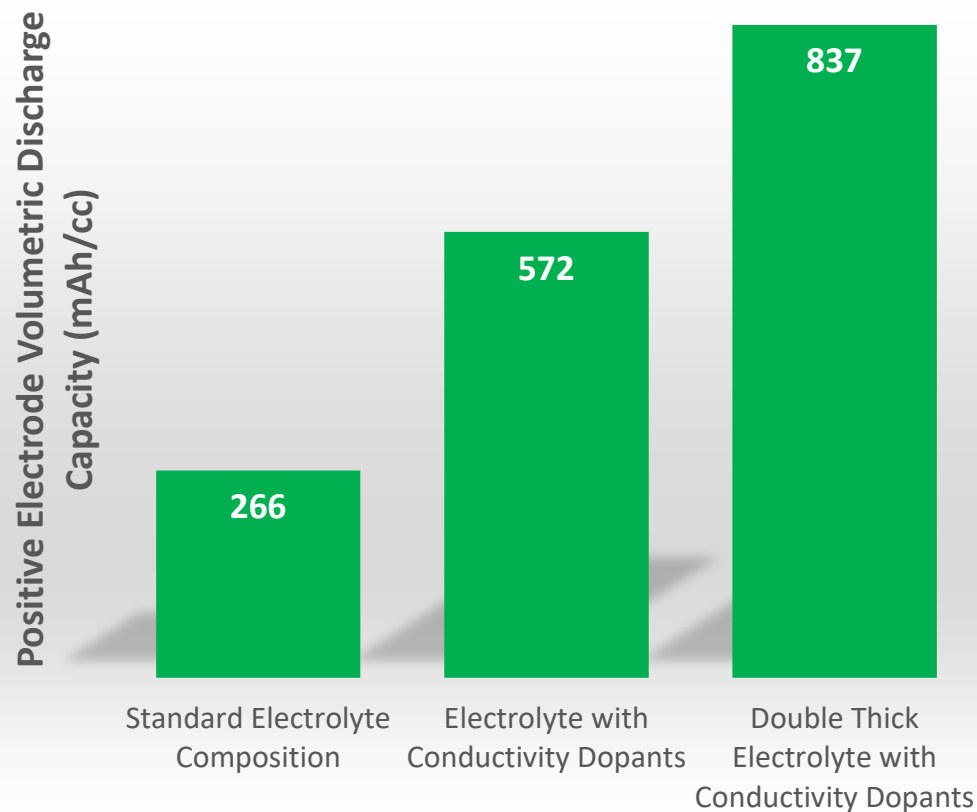
Improved Cell Performance Via Cell Design Modifications

- Formation Electrolyte Thickness
- Electrode Aspect Ratio
- Electrode Spacing



Complex interaction of transport pathways effect diffusion capabilities leading to better accessibility of the electrochemical active material

Electrolyte conductivity dopants previously enabled positive electrode capacity increase in single cells



➔ Conductivity dopants to be incorporated in 12 V cells to further increase utilization

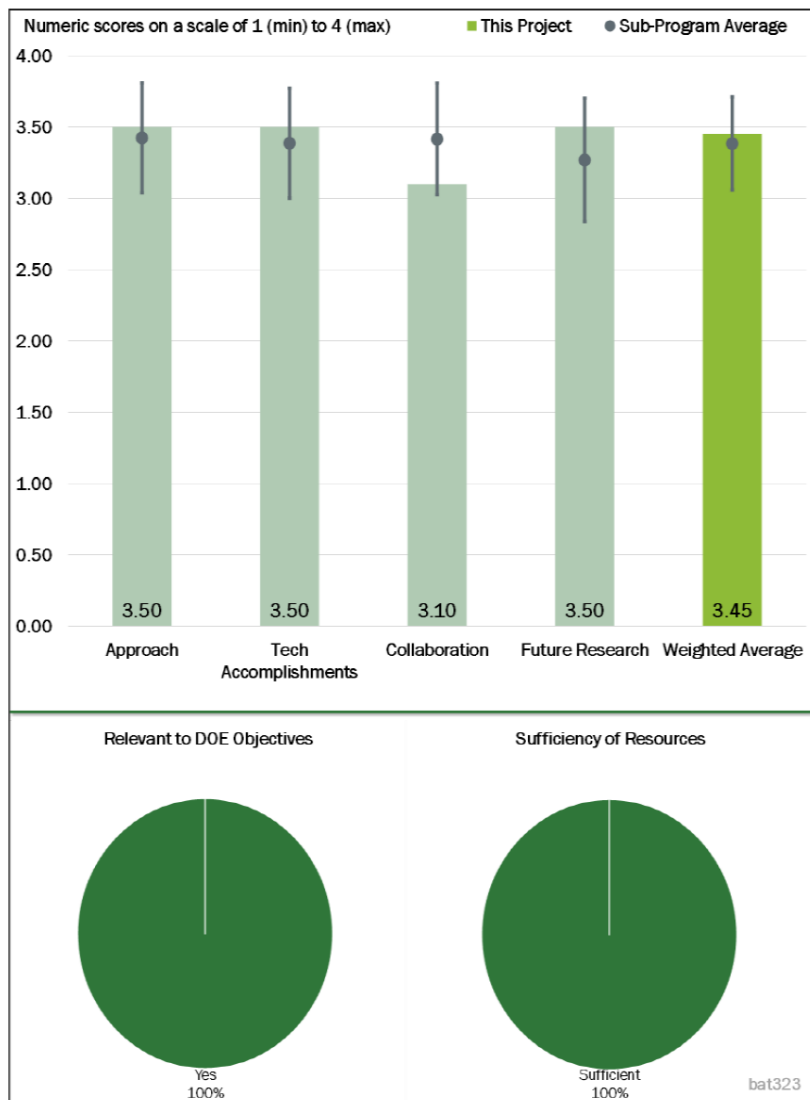


Figure 2-39 - Presentation Number: bat323 Presentation Title: Self-Forming Thin Interphases and Electrodes Enabling 3-D Structured High Energy Density Batteries Principal Investigator: Glenn Amatucci (Rutgers University)

- Comment:** Most reviewers concluded the program was well-designed and most barriers were addressed. One reviewers also commented that the chemistry is very challenging, very high risk and very high reward, which is what DOE should be funding.

Response: We thank the reviewers for their time and encouraging comments.

- Comment:** One reviewer expressed how the chemistry was never completely mapped and wondered if everything fell under “intellectual property”.
- Comment:** All reviewers acknowledged progress in realizing the key technical accomplishments. We also note that some reviewers requested more supporting data/graphs in the key accomplishments.

Response: The reviewer is correct and only limited information could be made public during the presentation. Most information will be made public in the future.

- **Comment:** *One reviewer noted the team needs to strengthen its collaboration in order to accomplish this project with more efficiency.*

Response: In concert with some of the other reviewers we believe that we currently do not need any active collaborators in this early high risk project due to the breadth and interdisciplinary of the internal Rutgers team. However, we plan on bringing on other teams when the project is further along and we will require other expertise that we do not have onsite.

- **Comment:** *All reviewers stated the proposed future work plan to be reasonable and with numerical targets that will help achieve the final goals.*

Response: We thank all the reviewers for their comments.

- **Comment:** *All reviewers found the project support the overall DOE objectives and that the available resources are adequate to achieve the stated milestones in a timely fashion*

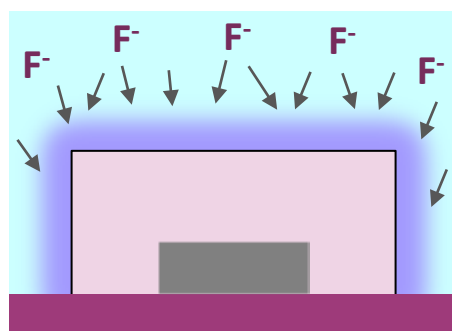
Response: We thank all the reviewers for their comments.



All work has been performed by the interdisciplinary team at Rutgers University

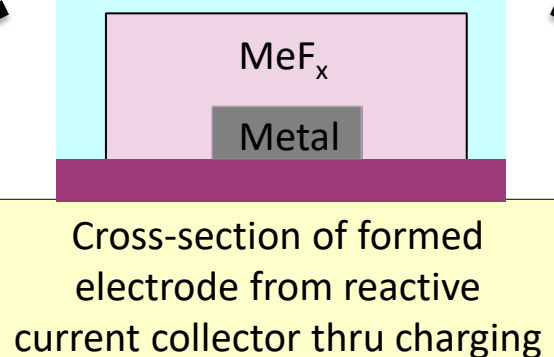
Increase in charge capacity \neq Improvements in discharge capacity

Ion Transport Limitation



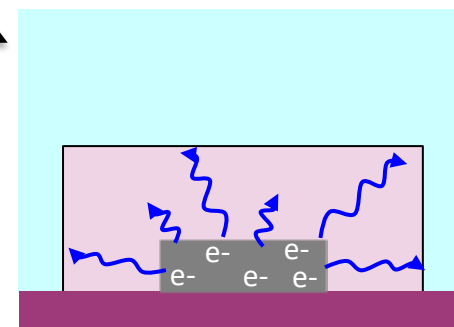
caused by deficient availability of F^- ions at electrode-electrolyte interface causing barrier in further electrolyte reaction

Formation Electrolyte



Cross-section of formed electrode from reactive current collector thru charging

Electron Transport Limitation



due to poor conductivity pathways through the reacted active material

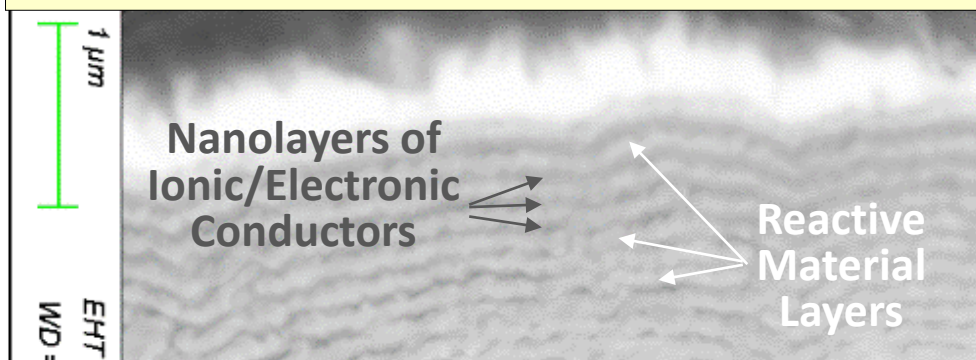
Capacity Loss

Limiting transport pathways lead to the development of inactive material areas resulting in capacity loss

Nanolayered electrodes with mixed conducting additives provide improved pathways for both ionic and electronic transport in isolated positive electrode studies

Positive Electrode Active Discharge Capacities	Standard Architecture	Multicomponent Mixed Conductor Architecture
Volumetric Capacity (mAh/cc)	340	598

Multicomponent Nanolayered Electrode Architecture



➔ Applying nanolayered mixed conductor architectures with cell design improvements to further propel transport properties leading to enhanced 12 V cell performance

- ***Identified transport pathways limiting performance advancement***
 - Ion transport limitation induced by F^- ion deficiency at electrolyte-electrode interface following extended charging causing loss of discharge capacity
 - Electron transport limitation caused by poor metal fluoride conductivity inhibiting electron transport from the current collector to the electrolyte-electrode interface
- ***Improved transport pathways for optimal access of active material through single cell electrode redesign***
 - Single cells showed an increase in capacities and electrode formation/ utilization improved by a factor 2.2 from 25% to 54% through
 - Modified electrode aspect ratio
 - Decreased electrode spacing
 - Incorporated nanolayered mixed conducting electrode architecture
- ***Developed & advanced 12 V cell configuration***
 - Successful formation and cycling of 12 V cell architecture
 - Fabrication of high energy density in-situ formed electrode pairs of up to 1059 Wh/L
 - Cell design optimization enabled significant increase in positive electrode utilization from 6% to 44% through the addition of excess electrolyte and the reduction of the cell dimensions